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Spectrally resolved thermoluminescence in UV excited hexagonal boron nitride nanopowder

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Abstract. Thermally stimulated luminescence (TSL) excitation and emission processes in h-BN nanopowders after UV irradiation were studied. TSL showed the highest response within the 5.4 eV band. 3.0 and 3.9 eV bands, resulting from the radiative donor-acceptor recombination between the electron (1B- и O_N-centers) and the hole traps (C_N-center), were found. TSL curves quantitative analysis in the context of general order kinetics was made. It was shown that 1B-centers had 0.85±0.05 eV activation energy and were responsible for the TSL peak at 350±10 K. Band structure for TSL excitation and emission mechanisms in h-BN nanopowder was suggested.

1. Introduction

Due to its unique electrophysical characteristics hexagonal boron nitride (h-BN) or “white graphite” is a promising base material for fabricating the Van der Waals heterostructures for the purposes of nano-, optoelectronics and nanophotonics [1, 2]. In addition, h-BN powders are used in the field of solid-state dosimetry of UV radiation [3, 23]. It is an indirect semiconductor with the band gap varying over the wide range and depending on the synthesis method, morphology, impurities composition, etc. [3, 4]. It is known that C and O are the main technological impurities in h-BN and can easily substitute B and N atoms in the crystalline lattice. Extrinsic defects and complexes based on them create the system of electron and hole traps in the band gap, affecting severely h-BN electrophysical and luminescent properties [5-7]. Spectrally resolved thermally stimulated luminescence (TSL) method is one of the direct methods to study fundamental processes of charge carrier traps. [8-10, 23].

Earlier [8, 23, 25] we showed that for h-BN micropowders with impurities C (2.9±0.3 at. %) and O (0.6±0.1 at. %) TSL peaks have their maximum at T_{max} =325, 360, 475 and 575 K in the emission bands of 330 nm (3.75 eV), 380 nm (3.26 eV) and 425 nm (2.92 eV). Researchs conducted earlier [20, 26] do not allow to determine fully the detected inhomogeneity of TSL spectral composition, as well as the number of peaks allowed in the TSL in known luminescence models and their nature. Thus, the study of nominally pure samples of h-BN (free of basic impurities) by the method of spectrally resolved TSL can provide new information and make the band scheme proposed by us earlier more precise [25]. Therefore, the aim of this work is to determine TSL energy and kinetic characteristics in hexagonal boron nitride nanopowder with a low content of C and O impurities irradiated by UV.



2. Sample and methods

The measurements were fulfilled for nominally pure h-BN nanopowder (Hongwu International Group Ltd., Hong Kong). C and O impurities content did not exceed 0.5 wt.% according to the manufacturer. It was found previously [11] that the nanopowder is mesographitic and demonstrates lognormal particles size distribution with the maximum of 225 nm.

TSL study was conducted using Perkin Elmer LS 55 spectrometer with the developed high-temperature accessory [8]. The temperature T of the samples varied from 300 to 750 K with the heating rate of $r=2$ K/s. TSL excitation spectra were measured in the range of $\lambda_{exc}=(200-380)\pm 5$ nm for irradiation wavelength and 10 nm step. Emission intensity was registered in $\lambda_{em}=390\pm 10$ nm band. Radiation dose was 9.0 mJ. Samples were irradiated with UV in $\lambda_{exc}=230\pm 5$ nm band with 4.5 mJ dose before the TSL emission spectra registration. TSL emission registration band varied in the $\lambda_{em}=300-600$ nm range with 10 nm step. As a result, 3D dependencies of TSL excitation and emission spectra were plotted.

3. Results

Temperature dependencies of the measured TSL excitation and emission spectra are presented in figure 1 as 3D graph projections in “ I intensity – λ wavelength – T temperature” coordinates system. It is seen, that spectral dependencies have complex shape with several defined peaks in $T=340-360$ K range. Exc1 peak (see figure 1a) is registered at $\lambda_{exc}\approx 230$ nm with $T_{max}\approx 353$ K and corresponds to the maximum of the most effective TSL excitation in the studied band. Exc2 and Exc3 peaks with the lower intensities are also registered in this temperature range at $\lambda_{exc}\approx 245$ and 310 nm with $T_{max}\approx 355$ and 357 K, accordingly. One intensive Em1 peak at $\lambda_{em}\approx 430$ nm with $T_{max}\approx 345$ K and one less intensive Em2 peak at $\lambda_{em}\approx 325$ nm and $T_{max}\approx 340$ K are registered for the TSL emission spectra (see figure 1b). In addition, the analysis of spectral and temperature cross-sections for observed 3D dependencies was performed.

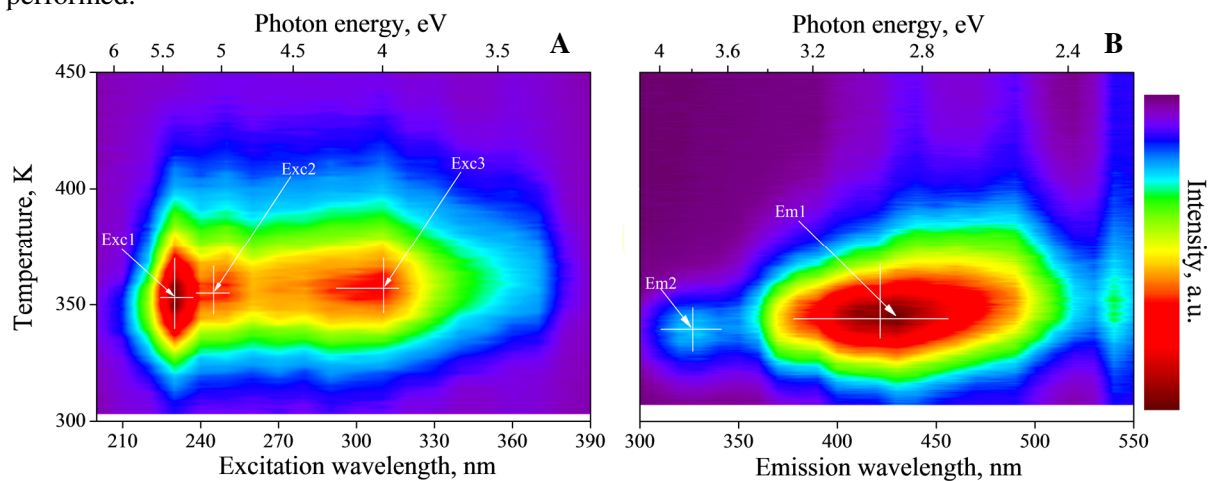


Figure 1. Contour profiles of TSL excitation (A) and emission (B).

4. Discussion

4.1. TSL excitation and emission spectra

Figure 2 shows normalized spectral dependencies at $T=353$ and 345 K of TSL excitation (a) and emission (b), correspondingly. The curves were approximated by the superposition of several Gaussians with satisfactory degree of accuracy (coefficient of determination $R^2 > 0.998$). The results are presented in table 1.

Analysis of all deconvolutions in the studied temperature range has shown that TSL excitation spectra has three Exc1, Exc2 and Exc3 components (see figure 2a) with $E_{max} \approx 5.4$, 5.0 and 4.2 eV energies and $\omega_E \approx 0.4$, 0.6 and 1.0 eV halfwidths, accordingly. Excitation bands under discussion were registered earlier in the h-BN luminescent properties study [5, 11, 13-17]. Literature review has shown that E_{max} of Exc1 band can correspond to the band gap $E_g = 5.27-5.82$ eV, determined by diffuse reflection (DR) and optical absorption (OA) [11, 13-16]. Exc2 and Exc3 bands could be attributed to intrinsic and extrinsic defects of h-BN crystalline lattice [5, 17]. For example, through the excitation of carbon impurity centers and its ionization processes [17], and the transition of charge carriers from the valence band to the deep trapping level [5].

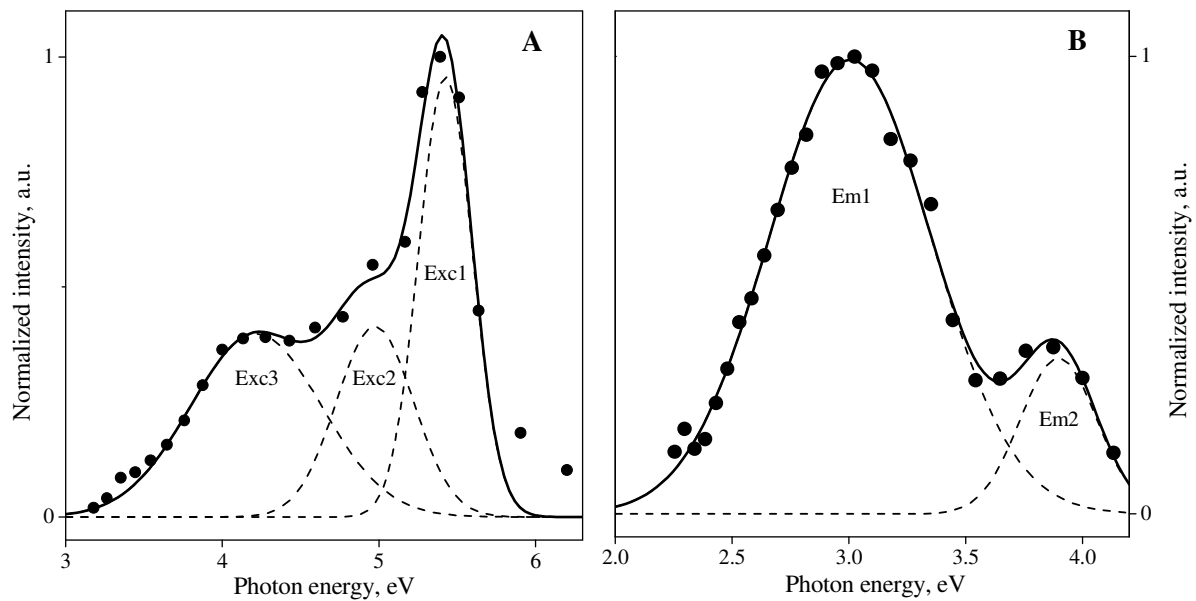


Figure 2. TSL excitation (A) and emission (B) spectra at $T=353$ and 345 K, accordingly. symbols – experiment, dash lines – components, solid line – approximation.

Table 1. Parameters of h-BN TSL excitation and emission spectra approximations.

Type of spectrum	T (K)	Peak	Parameter			Other works			
			$I, \pm 0.1$ (a.u.)	$E_{max}, \pm 0.1$ (eV)	$\omega_E, \pm 0.05$ (eV)	E_{max} (eV)	Technique	Defect	Reference
Excitation	353	Exc1	0.96	5.43	0.40	5.27-5.82 5.41	OA, DR DR	Direct forbidden gap	[13-16] [11]
		Exc2	0.41	4.97	0.58	4.6-4.8	PL	$VB \rightarrow V_N$	[5,17]
		Exc3	0.40	4.22	0.98	4.1	PL	C_N	[17]
Emission	345	Em1	0.99	3.01	0.81	2.9-3.0 2.9	PL, CL	V_N or O_N $V_N, 2-V_N, 3-V_N$	[18, 19] [20]
		Em2	0.34	3.89	0.39	3.64-3.85 3.75	CL TSL	C_N or O_N 1B and C_N	[6, 22] [25]

In TSL emission spectra there are two Em1 and Em2 bands with $E_{max} \approx 3.0$ and 3.9 eV, $\omega_E \approx 0.4$ and 0.8 eV, correspondingly. It should be noted that Em1 band dominates and does not change under the temperature variation in the studied range. The comparison with independent results has shown that Em1 band is typical for the nanostructured state of h-BN [5, 18, 19]. Emission in this range is usually attributed to V_N nitrogen vacancies or O_N extrinsic oxygen vacancies [18]. At the same time, emission with close parameters is registered in cathodo- (CL) and photoluminescence (PL) spectra of h-BN nanostructures [3, 19-23], films [24] and single crystals [6]. It is supposed that the discussed band relates to C_N extrinsic centers [6, 22] or V_N , $2-V_N$, $3-V_N$ nitrogen vacancies [20].

4.2. TSL curves numeric analysis

General order kinetic equation [12] was used to quantitate experimental TSL-curves:

$$I = s'' n_0 \exp\left(-\frac{E_a}{kT}\right) \left(1 + \frac{s''(b-1)}{r} \int_{T_0}^T \exp\left(-\frac{E_a}{k\theta}\right) d\theta\right)^{-\frac{b}{b-1}} \quad (1)$$

s'' – effective frequency factor, s^{-1} ; n_0 – initial concentration of trapped charge carriers in traps, m^{-3} ; E_a – trap activation energy, eV; k – Boltzmann constant, eV/K; b – kinetic order; r – heating rate, K/s.

Approximation parameters are presented in table 2. Figure 3 shows the examples of TSL emission spectral dependencies approximation in $\lambda_{em}=430$ and 320 nm bands for Em1 and Em2 peaks, respectively. According to figure 3 and table 2 all observed TSL curves can be described well by a single component of general order kinetics.

Table 2. Kinetic parameters of h-BN TSL curves.

Parameters	Exc1	Exc2	Exc3	Em1	Em2
$\lambda_{exc}/\lambda_{em}$ (nm)	230/390	240/390	310/390	230/430	230/320
$T_{max}, \pm 2$ (K)	353	355	357	345	339
$E_a, \pm 0.01$ (eV)	0.82	0.82	0.80	0.88	0.88
$s'', \pm 10\%$ (s^{-1})	$6.3 \cdot 10^{10}$	$5.7 \cdot 10^{10}$	$2.8 \cdot 10^{10}$	$1.6 \cdot 10^{12}$	$2.4 \cdot 10^{12}$
$b \pm 0.1$	2.5	2.6	2.6	2.4	1.5
R^2	0.998	0.997	0.997	0.996	0.994

It can be concluded that the observed thermally stimulated emission with $T_{max}=340-360$ K of h-BN sample is attributed to charge carriers traps with $E_a=0.85 \pm 0.05$ eV activation energy and $s''=2 \cdot 10^{10}-3 \cdot 10^{12} s^{-1}$ effective frequency factor. Kinetics order of $b \approx 2.5$ shows that processes of carriers recapturing responsible for registered TSL in $T=300-400$ K range dominate. Therein, observed variations for T_{max} and s'' of TSL curves are due to registration conditions (emission band and radiation dose). The calculated E_a values correspond to the independent data for 1B-center characterized by $E_a=0.7$ eV [25, 26]. It is supposed that 1B-center is V_N defect based on nitrogen vacancy and is formed in presence of oxygen [26].

4.3. TSL mechanisms

The observed spectral and kinetic TSL features of studied h-BN nanopowder can be characterized in framework of proposed earlier in [25] band scheme. According to the model emission in Em1 (≈ 3.0 eV) the band is resulted from radiative donor-acceptor recombination between the electron trap (1B-center with $E_a=0.8-0.9$ eV) and the hole trap (C_N -center with $E_a=1.4$ eV [26, 27]). Following the same logic, it can be supposed that emission in Em2 (≈ 3.9 eV) is due to the donor-acceptor recombination between O_N -center with $E_a \approx 0.3$ eV [26] and C_N -center. Then, E_a corresponds to difference between emission energies in Em2 and Em1 bands. Value of $E_a=0.8-0.9$ eV is an activation energy of the trap respectively to the O_N -centers levels forming, as known, sub-band of the allowed energy states close to the bottom of conducting band in h-BN [27]. Following points can be substantiated

according to the TSL excitation analysis. Firstly, Exc1 (≈ 5.4 eV) excitation band can be attributed to band gap of studied sample and Exc2 (≈ 5.0 eV) band – to electron transition from valence band (VB) to O_N -center level. Secondly, Exc3 (≈ 4.2 eV) band can be resulting from electron transition either from valence band to 1B-center level or from C_N -center to conducting band (CB). The processes of TSL excitation and emission described above are shown in figure 4.

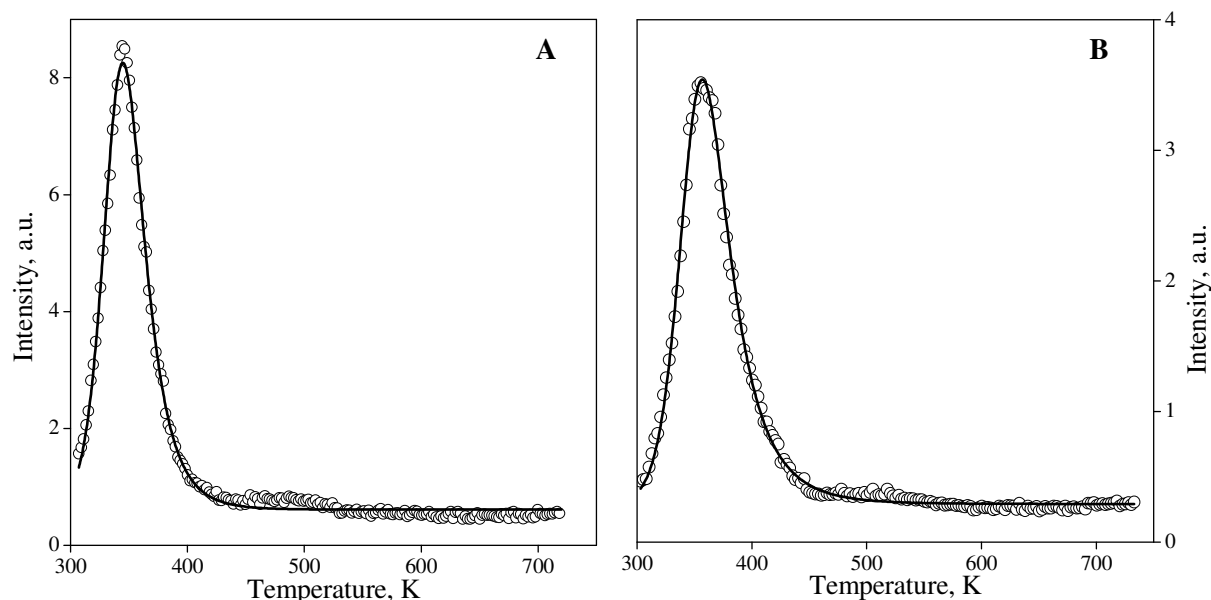


Figure 3. TSL curves in Em1 (A) and Em2 (B) emission bands.
Symbols – experiment, solid line – approximation

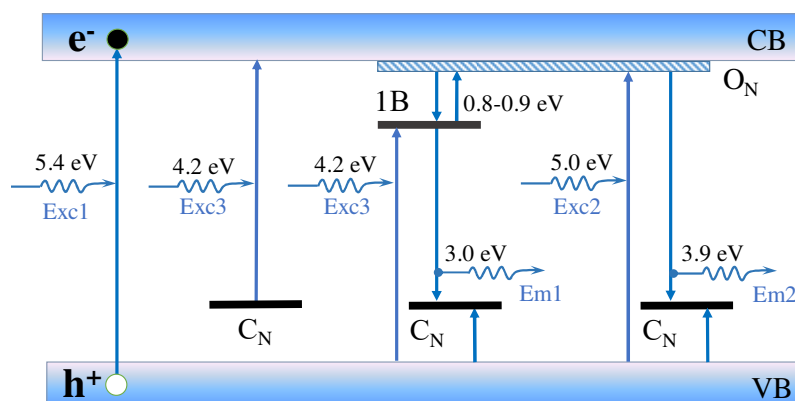


Figure 4. Band scheme of TSL processes in h-BN.

5. Conclusion

The current work contains the studies of thermally stimulated luminescence processes of hexagonal boron nitride nanostructured powder. TSL excitation and emission spectra after UV irradiation were measured. It was found that the 3.0 eV band with 0.8 eV halfwidth dominated in the TSL emission. Also, the 3.9 eV band was registered. The highest TSL response was registered after the irradiation of studied powder with 5.4 eV photons.

TSL curves were analyzed in the 300–750 K range in the context of general order kinetics. It was shown that TSL response had maximum in the 350 ± 10 K range and is formed due to the emptying of the trap with $E_a = 0.85 \pm 0.05$ eV activation energy. Kinetics order demonstrated $b \approx 2.5$ values that can be attributed to prevalence charger carriers recapturing process in traps responsible for registered TSL in 3.0 eV band and $T = 300$ –400 K temperatures. The band scheme explaining registered TSL mechanisms with participation of O_N^- , $1B^-$ и C_N^- -centers, based on the obtained data and the literature review of thermal and photostimulated processes in h-BN, was suggested

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